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PRODUCTION OF A COMPLEX NITRIDE-CONTAINING MIXTURE BY OXIDATION OF ZIRCONIUM AND ALUMINUM IN AIR

A. P. Il'in,[1] V. V. An,[1] V. I. Vereshchagin,[1] and G. V. Yablunovskii[1]

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The authors investigate the chemical composition of the combustion products of mixtures of a freely poured industrially produced zirconium-aluminum alloy powder (84 wt.% zirconium) and an ultradisperse aluminum powder produced by electric detonation of conductors in argon. It is established that under certain conditions the end products can contain up to 60% AlN + ZrN mixture.

There is currently a demand for ceramic materials based on high-melting nitrides. This is due to the fact that these compounds have a number of valuable properties that make them suitable for use under severe conditions, namely, at high temperatures and in aggressive environments. These materials include aluminum nitride, which exhibits high thermal conductivity, heat resistance, and specific electrical resistance and is resistant to the action of aluminum melts [1]. Therefore, the development of new methods for nitride production that are alternative to traditional methods becomes an important problem.

The experiments described in [2] were carried out to obtain a nitride-containing batch using a method based on the effect of chemical binding of air nitrogen in oxidation of an ultradisperse aluminum powder (UDAP) [3]. It was reported [2] that due to a shortage of UDAP it was diluted with industrially produced ASD-1 powder. The effect observed in this case was the same as when UDAP without additives was used.

For the purpose of verification, this method of binding air nitrogen was tested in production of other high-melting nitrides, in particular, zirconium nitride. In addition to infusibility zirconium nitride has high electrical conductivity and arc resistance [4]. It was obtained in oxidation of zirconium-containing powders in air, since pure zirconium is extremely pyrophobic, and its use is undesirable.

The present paper describes results of experiments carried out on mixtures of UDAP and an industrial zirconium-aluminum alloy (zial) powder whose weight content of aluminum was 16% and average particle diameter was < 40 μm. The zial content in the initial mixtures was varied from 20 to 60%. Combustion of cone-shaped batches (5 g each), as in [2], was initiated by transmitting an electric-current pulse through a Nichrome spiral. Temperature readings in the combustion zone were recorded using a standard Chromel-Alumel thermocouple (a conductor diameter of 0.5 mm) and a KSP-4 recorder. The thermocouple junction was protected from the action of active aluminum vapor by a corundum cap.

Figure 1 shows the dependence of the temperature in the combustion zone on the zial content in the initial mixtures. It is seen that an increase in the zial content correlates with an increase in the maximum temperature of powder combustion. Moreover, compared to mixtures of UDAP and ASD-1 powder, the combustion process of zirconium-aluminum powders had a very short first stage: this process passed virtually at once to the second, high-temperature stage and was accompanied by brighter luminosity.

The sintered cakes obtained were crushed and subjected to an x-ray phase analysis. According to data of the x-ray phase analysis, AlN, ZrN, α-Al_2O_3, ZrO_2 (monoclinic),

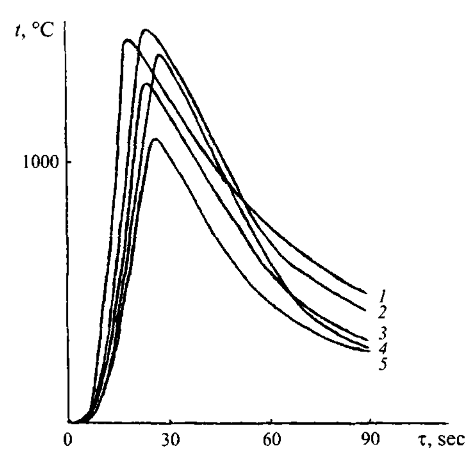

Fig. 1. Dependence of the temperature in the combustion zone on the zial content in the initial mixture: *1*) 50%; *2*) 40%; *3*) 30%; *4*) 20%; *5*) 10%.

[1] Research Institute of High Voltages at Tomsk Polytechnic University, Tomsk, Russia.

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TABLE 1

Sample	Mass content in initial mixture, %		Mass content of bound nitrogen, %
	UDAP	zial	
1	40	60	10.6
2	50	50	14.6
3	60	40	15.3
4	70	30	15.8
5	80	20	16.1
6	90	10	16.6

TABLE 2

Sample	Mass content, %						
	AlN*	ZrN*	AlN+ZrN*	Al_2O_3 ($\alpha + \gamma$)	ZrO_2	Al**	remainder***
1	20.3	27.4	47.7	24.2	17.8	7.3	3.0
2	32.3	27.0	59.3	27.3	8.4	1.6	3.4
3	35.2	24.4	59.6	29.7	3.2	4.1	4.1
4	39.9	16.5	56.4	32.7	3.7	4.9	4.9
5	44.3	7.9	52.5	36.5	4.8	5.2	5.2

* The sum found from chemical analysis for nitrogen, the ratio between the nitrides found from thermogravimetric data.
** From thermogravimetric and DTA data.
*** Sorbed gases, water, and other volatile impurities.

AlON, and Al were identified among the combustion products. With a decrease in the zial content in the initial mixtures, a decrease in the intensity of 100% ZrN reflections and, conversely, an increase in the reflections of AlN intensity were observed. According to DTA data, combustion products that formed under high-temperature conditions are oxidized with an increase in mass under subsequent heating in air at a temperature of 600 – 700°C.

As the mass content of UDAP in the initial mixtures increases, the amount of residual metallic aluminum in the combustion products increases, which is probably related to the different oxidation conditions of ultradisperse aluminum and aluminum in the form of a solid solution with zirconium. Aluminum is usually oxidized with formation of an almost impermeable oxide film on the particle surface, which slows down the oxidation process. In heating and oxidation, melted aluminum particles actively coalesce and form large drops. Oxidation of large aluminum drops proceeds according to a diffusion mechanism. An increase in the oxidation rate is possible when the oxide-film continuity is disrupted. One of the mechanisms responsible for film destruction is embrittlement caused by introduction of additives into the aluminum [5].

In our case, disruption of the continuity of the film of oxidation products in oxidation of UDAP is related to the interaction between the aluminum oxide and the aluminum with formation of a volatile suboxide. Moreover, formation of independent nitride phases that differ from oxides in their thermophysical parameters also facilitates cracking of the oxide-nitride film. The film that is formed in oxidation of zial is heterophase and permeable to gases, and therefore the process of alloy oxidation proceeds more intensely. The high rate of zial oxidation is due to the absence of a continuous film of combustion products, and the zial oxidation process proceeds to completion, since no zial reflections are recorded in the x-ray patterns of the combustion products. Thus, the degree of zial conversion is higher than the degree of UDAP conversion due to the heterogeneity of its combustion products.

The content of bound nitrogen in the combustion products of UDAP-zial mixtures was determined using the Kjeldahl method (Table 1). Batch samples with a higher UDAP content contain more bound nitrogen; in combustion of a mixture with a ratio of UDAP and zial equal to 40 : 60 the nitrogen content was 10.6%, and for a ratio of UDAP : zial = 80 : 20, the nitrogen content increased to 16.6%. It should be noted that with an increase in the zial content in the initial sample (according to data of an x-ray phase analysis and a DTA) the content of ZrN in the products increases. This points to the fact that the efficiency of binding air nitrogen (the ratio of nitride : initial metal) in oxidation is lower in UDAP than in zirconium, but the total content of nitrides passes through a maximum, attaining nearly 60%, due to the difference in the atomic weights of aluminum and zirconium. The chemical composition of the nitride-containing batches, which are the end products of combustion of UDAP with zial in air, is given in Table 2.

Thus, combustion of mixtures of UDAP with zial (zirconium content 84%) in air makes it possible to obtain a batch that contains up to 60% AlN + ZrN for certain ratios of the powders (50 – 60% UDAP).

The total content of bound nitrogen can be varied from 10 to 16.6% by varying the content of zirconium (zial).

Since the method of binding air nitrogen in combustion is fairly simple, it can be used to produce nitride-containing batches of aluminum and zirconium.

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